

# 193 nm Photodissociation of Thiophene Using Synchrotron Radiation

Fei Qi, Osman Sorkhabi, Abbas H. Rizvi, and Arthur G. Suits

*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720*

## INTRODUCTION

Thiophene is a five-membered heterocyclic compound with a sulfur atom. The photodissociation study of thiophene is important in fossil fuel combustion, molecular biology and material science.<sup>1</sup>

Several gas phase photodissociation studies have been done on thiophene.<sup>2-6</sup> Ng and co-workers examined the isomeric structures of photofragments formed in the 193 nm photodissociation of thiophene using photodissociation-photoionization and 2 + 1 REMPI experiments<sup>5</sup> Only two dissociative channels,  $C_2H_2S + C_2H_2$  and  $C_4H_4 + S$ , were identified by Ng and co-workers. They found that the S atoms were produced predominantly ( $\geq 96\%$ ) in the  $^3P_J$  states. Using photofragment translational spectroscopy, Mayers et al. performed the first direct examination of primary photoproducts of thiophene at 193 nm. Six primary dissociative channels were identified.<sup>6</sup>

In this study, we have measured the time-of-flight spectroscopy and photoionization efficiency spectra (PIE) of photofragments from the photolysis of thiophene using photofragment translational spectroscopy and undulator synchrotron radiation from the Chemical Dynamics Beamline at the Advanced Light Source.

## EXPERIMENTAL

The experiment was completed at beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere.<sup>7</sup> A pulsed molecular beam of 10% thiophene seeded in helium was skimmed twice and intersected at  $90^\circ$  with the photolysis laser (193.3 nm, Lambda Physik LPX 220I). Photofragments formed by 193 nm photodissociation entered the detector chamber region ( $2 \times 10^{-10}$  Torr) and were photoionized using tunable synchrotron radiation. The tunability of the light source allows for selective ionization of products and very low background counts, permitting the measurement of the PIE spectra of photofragments. The photoionized products were mass selected by using a quadrupole mass filter and the ions were counted with a Daly ion counter. A multi channel scalar (MCS) was used to measure the time-of-flight (TOF). Thiophene (99%) was obtained from Aldrich and used without further purification.

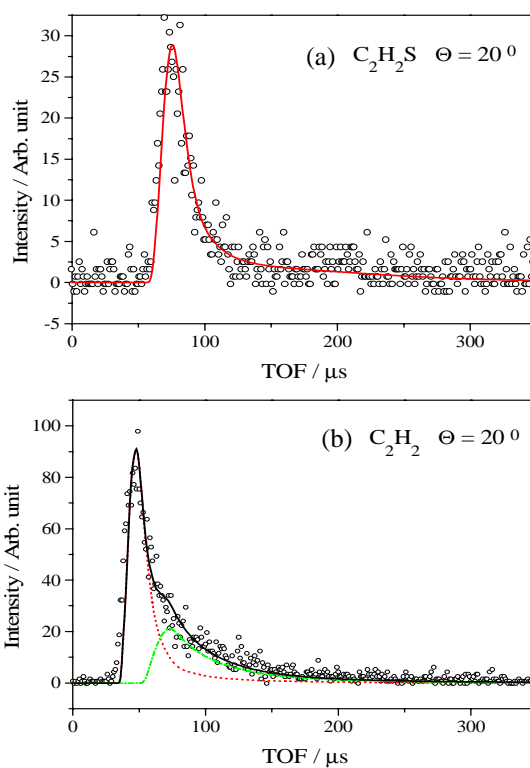
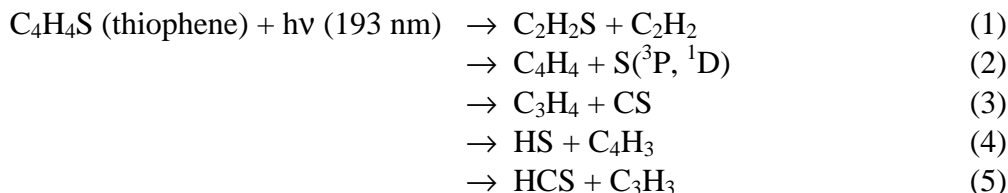


Fig. 1 (a) The mass 58 ( $C_2H_2S$ ) TOF spectrum at  $20^\circ$ . The data is presented by circles. The black line is the fit to the data using the P(E) shown in Fig. 2(a); (b) The mass 26 ( $C_2H_2$ ) TOF spectrum at  $20^\circ$ . The black line is the fit to the data using the P(E) (dash line) from Fig. 2(a) and The P(E) (dot-dash line) from Fig. 2(b).

## RESULTS AND DISCUSSION

The TOF spectrum at  $m/e$  58, 52, 51, 45, 44, 40, 39, 33, 32, and 26 have been done at different angles (20 - 50°). Five primary dissociative channels have been identified, including three closed shell channels and two radical channels, as summarized by processes 1-5.



Similar channels, (1) (4) and (5), were observed in the dissociation of furan at 193 nm.<sup>8</sup> Two additional channels (2) and (3) were observed in this study because the C-S bond is weaker than C-O bond in furan. Fig. 1(a, b) shows the Time-of Flight (TOF) spectrum of  $\text{C}_2\text{H}_2\text{S}$  and  $\text{C}_2\text{H}_2$  at 20°. Some of the  $\text{C}_2\text{H}_2\text{S}$  fragments were found to undergo secondary dissociation. Fig. 2(a) shows the translational energy distribution  $P(E)$  of the  $\text{C}_2\text{H}_2\text{S} + \text{C}_2\text{H}_2$  channel, which is used to fit Fig. 1(a) data. The  $\text{C}_2\text{H}_2$  TOF spectrum, however, needs another contribution [shown in Fig. 2(b)] besides the  $P(E)$  of Fig. 2(a). The  $P(E)$  shown in Fig. 2(b) corresponds to secondary dissociation of  $\text{C}_2\text{H}_2\text{S}$  to  $\text{C}_2\text{H}_2 + \text{S}$ . This secondary dissociation was not observed in Mayers' study.<sup>6</sup> By measuring the PIE spectra of mass 58 and 22, the isomeric structures of the fragment  $\text{C}_2\text{H}_2\text{S}$  and  $\text{C}_2\text{H}_2$  were determined to be that of thioketene ( $\text{CH}_2=\text{C}=\text{S}$ ) [the PIE spectroscopy of the mass 58 shown in Fig. 3] and acetylene, respectively. Our results are in good agreement with previous studies.<sup>5</sup> The  $P(E)$  shown in Fig. 2(a) indicates the presence of a barrier of at least

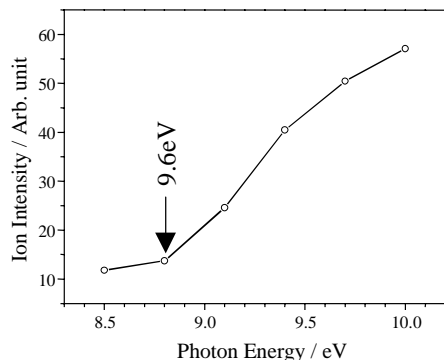


Fig. 3 Photoionization efficiency spectroscopy of the  $\text{C}_2\text{H}_2\text{S}$  fragment.

16.5 kcal/mol for this process. Preliminary analysis indicates that the closed shell channels occur on the ground state potential energy surface following internal conversion. Furthermore, it is believed that the dissociation of thiophene at 193 nm involves the formation of the biradical  $\bullet\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{S}\bullet$  as the initial step. The rapid decomposition of this biradical may yield different channels.

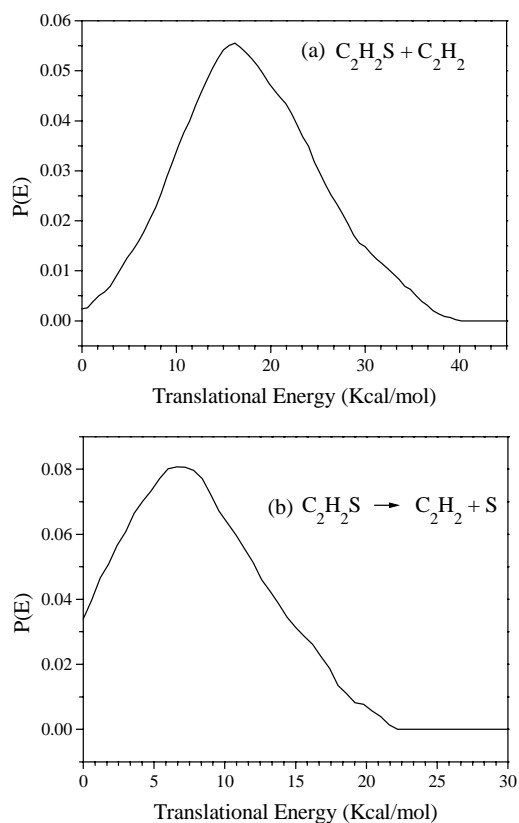


Fig. 2 (a) The translational Energy Distribution  $P(E)$  of  $\text{C}_2\text{H}_2\text{S} + \text{C}_2\text{H}_2$ ; (b) The translational Energy Distribution  $P(E)$  of  $\text{C}_2\text{H}_2\text{S} \rightarrow \text{C}_2\text{H}_2 + \text{S}$ .

The other fragments were identified as vinyl acetylene ( $C_4H_4$ ,  $H_2C=CH-C\equiv CH$ ), 1-2-propadiene ( $C_3H_4$ ,  $H_2C=C=CH_2$ ), and propargyl radical ( $C_3H_3$ ,  $HC\equiv C-C^\bullet H_2$ ). Preliminary analysis indicates that sulfur is produced in both the  $^3P$  and  $^1D$  electronic states

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Principal investigator: Arthur G. Suits, Chemical Sciences Division, Lawrence Berkeley National Laboratory.  
E-mail: AGSuits@lbl.gov. Telephone: 510.495.4754.